A new solution combustion route to synthesize LiCoO$_2$ and LiMn$_2$O$_4$

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Abstract

Commercially important, high-voltage, lithium cathodes, such as LiCoO$_2$ and LiMn$_2$O$_4$ have been synthesized from nitrates, following the 'soft-chemistry' approach using starch as the combustion-assisting component. The minimum temperature required for phase formation and the degree of crystallinity has been evaluated from thermal studies and X-ray diffraction analysis, respectively. The starch-assisted combustion (SAC) method produces mono-dispersed powders of grain size below 1.5 μm as observed from scanning electron microscopy and particle-size analysis. The electrochemical activity of the synthesized oxide powders has been examined via cyclic voltammetric and charge–discharge studies using lithium coin cells.

Cyclic voltammetric data shows excellent reversibility with respect to Li$^+$ and confirms the effect of crystallinity of the compounds on the electrochemical performance of the cathode materials. The electrochemical stability and performance of the cathodes over 30 cycles have been demonstrated with a capacity fade of <10% of the initial capacity. The simplicity and flexibility of this approach towards the synthesis of various other cathode materials is also discussed.
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Keywords: Starch-assisted combustion synthesis; Electrochemical activity; Crystallinity; LiCoO$_2$; LiMn$_2$O$_4$; Lithium cathodes

1. Introduction

Today's world of modernization and miniaturization lays a greater emphasis on more power from smaller and lighter battery packs. In this regard, lithium batteries are in greater demand for powering smaller, lighter and portable consumer electronic devices [1] in such batteries, battery-active lithiated transition metal oxide is used as the positive electrode (cathode). Generally, the battery activity of any cathode is governed by its chemical composition, stoichiometry, phase homogeneity, crystallite size, etc. These aspects clearly depend on the nature of the precursors selected and methods adopted for the synthesis [2]. Hence, an unabated interest has been shown by both the academic and the commercial sectors towards the selection of materials, mode of synthesis and improvement in synthetic strategies for preparing cathodes for lithium cells. Though a large number of transition metal oxides have been proposed as possible electrode materials for high-voltage lithium batteries, attention has mainly been focused on LiCoO$_2$ [3] and LiMn$_2$O$_4$ [4], primarily because of their ease of synthesis in the laboratory as well as on an industrial scale.

Literature is replete with the methods of synthesis of these materials that employ various precursors and heating procedures with variation in temperature, reaction time, atmosphere, etc. [5]. The standard approach towards synthesizing the cathode samples, namely, the solid-state method, usually requires a long heating time and high temperatures. Firing at high temperatures, however, induces crystallite growth which, in turn, causes adverse effects on the electrochemistry of the materials. In other words, the formation of large crystallites tend to lower the kinetics of diffusion. As a result, polarization is increased during charge/discharge, and thus reduces workability of the cathode. By contrast, smaller particles result in better cycleability, charge retention, and smaller IR drop. Therefore, particle-size has a direct influence on the electrochemical performance of the cell [6]. Moreover, high-temperature processing may lead to lithium loss [7] and thereby affects the stoichiometry and structural characteristics of the compound. Hence, it is essential to identify an ideal methodology that can result in the formation of stoichiometric compounds with good control over the chemistry, purity, morphology, etc. of the crystals.

In this paper, we describe a simple soft-chemistry synthesis scheme for 4 V LiCoO$_2$ and LiMn$_2$O$_4$ that follows the so-called starch-assisted combustion (SAC) method. The novelty of this method has already been investigated and reported with respect to the synthesis of the 4.8 V system,
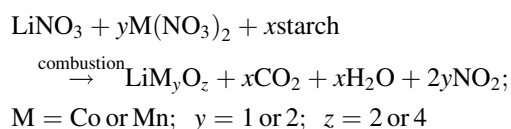
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namely, LiNiVO$_4$ [8]. The SAC method has advantages of being a single-step process with good product yield, relatively short processing time at moderate temperature, high chemical homogeneity and mono-dispersed particles of sub-micron size and large surface area which leads to better electrochemical performance. The significance of the SAC method to synthesize any type of high-voltage cathode material for lithium batteries has also been examined.

2. Experimental

2.1. Synthesis of LiCoO$_2$ and LiMn$_2$O$_4$

Crystalline powders of LiCoO$_2$ and LiMn$_2$O$_4$ were synthesized from the combustion of an aqueous mixture containing stoichiometric amounts of lithium nitrate and the respective metal nitrates along with starch. Starch was added to assist combustion, the amount of which was determined by a trial-and-error method [8]. The resulting solutions were evaporated to dryness at 110 °C and gave a highly raised foam (precursor). The foam was decomposed at 250 °C for 3 h to expel carbon in the form of CO$_2$ that results from the combustion of starch–nitrate mixture. The resulting brown-black mass was subsequently heated from 300 to 700 °C for 3 h. All thermal treatment was performed in air only. A schematic approach of the starch-assisted route is clearly depicted in the flow chart shown Fig. 1. The compound formation is expected to occur according to the following empirical equation:

$$LiNO_3 + yM(NO_3)_2 + x\text{starch}$$

$$\xrightarrow{\text{combustion}} LiM_yO_z + xCO_2 + xH_2O + 2yNO_2;$$

$$M = Co \text{ or } Mn; \quad y = 1 \text{ or } 2; \quad z = 2 \text{ or } 4$$

2.2. Instruments

Thermal studies thermal gravimetric (TG)/differential thermal analysis (DTA) were carried out in air at a heating rate of 10 °C min^{-1} using a simultaneous thermal analyzer (model number STA 1500, PL Thermal Sciences, UK). The phase purity of the products was verified using a JEOL-JDX 8030 X-ray diffractometer. The diffractograms were recorded using nickel-filtered Cu Kα radiation ($\lambda = 1.5406$ Å) at room temperature in the 2θ range 10–80° with a scan rate set at 0.1° s^{-1}. FTIR spectra of the compounds were recorded on a Perkin-Elmer Paragon-500 EFIR spectrophotometer in the range 400–1000 cm^{-1} using KBr pellets. Powder densities were measured by means of Archimedes' principle, using xylene as the liquid medium. The morphology of the powders was examined with a HITACHI S-3000 H scanning electron microscope and the particle-size distribution was determined by a malvern easy particle sizer, based on laser diffraction. The surface area of the synthesized powders was determined by BET adsorption method using low temperature nitrogen adsorption (Quanta Chrome
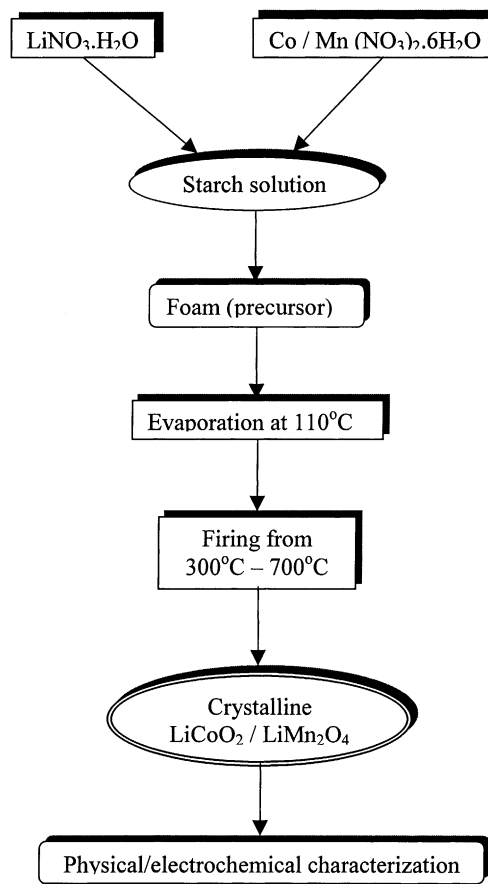

Fig. 1. Flowchart showing various steps involved in starch-assisted-combustion synthesis of LiCoO$_2$ and LiMn$_2$O$_4$.

Nova 1000, US). The stoichiometry of the compounds was verified with a atomic absorption spectrophotometer (Spectra 220, Varian, Australia).

Electrochemical performance was evaluated by assembling cathode-limited 2016 lithium coin cells. The cathodes were fabricated by slurrying the cathode powders with 10 wt.% graphite and 2 wt.% poly(vinylidene fluoride) (PVdF) as binder in N-methyl 2-pyrrolidone (NMP) as solvent and coating the mixture over aluminum foil (serves as a current-collector). After drying at 110 °C overnight, discs of 1.6 cm diameter were punched out and weighed. Typical cathodes were found to have a coverage of about 12 mg of active material. The elctrolyte consisted of 1 M LiAsF$_6$ 1:1 (v/v) ethylene carbonate (EC):dimethyl carbonate (DMC). Charge/discharge studies were performed using an in house cell testing unit. Cyclic voltammograms were recorded with 'AUTOLAB' software governed by a personal computer.

3. Results and discussion

3.1. Thermal analysis of LiCoO$_2$ and LiMn$_2$O$_4$

The TG/DTA curves for LiCoO$_2$ and LiMn$_2$O$_4$ are shown in Fig. 2(a) and (b), respectively. A single exothermic peak
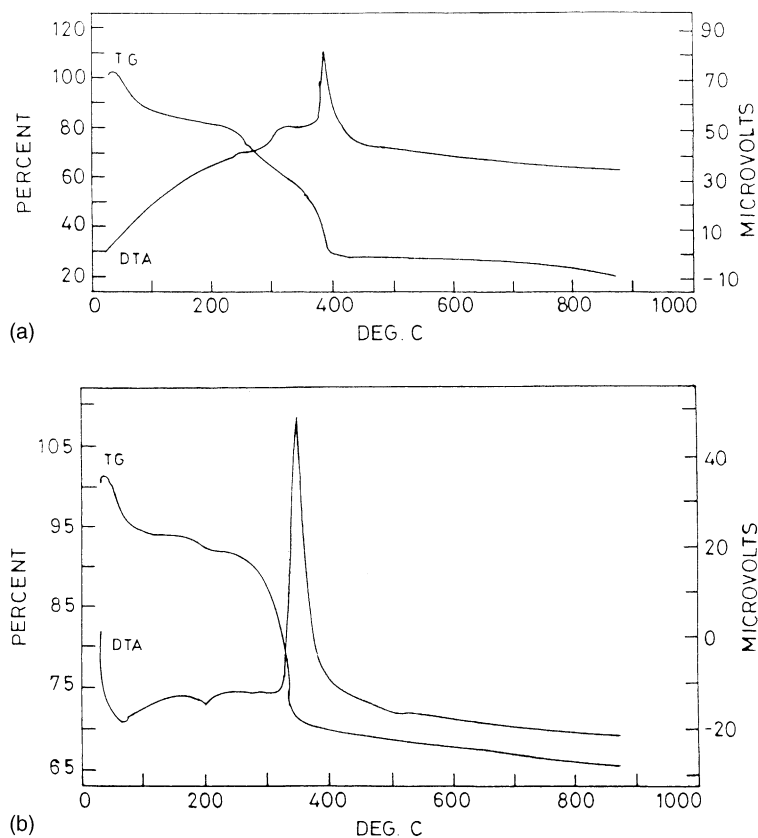
Fig. 2. (a) TG/DTA of LiCoO$_2$ at 10 °C/min rate. (b) TG/DTA of LiMn$_2$O$_4$ at 10 °C/min rate.

observed around 385 °C for LiCoO$_2$ and 340 °C for LiMn$_2$O$_4$, which indicate the completion of combustion of the starch–nitrate precursors. During the decomposition process, a great deal of energy, equivalent to the (sum of) dissociation energies of C–C (304 KJ/mol), C–H (413 KJ/mol) and C–O (358 KJ/mol) bonds [9], is expected to be released. The process of phase evolution takes place at a temperature well below 400 °C, which is established from the X-ray diffraction results. As the decomposition proceeds, however, it is believed that the formation and crystallization of the oxides occur consecutively.

Beyond this temperature, no further mass loss has been observed in the TG/DTA diagram up to 700 °C (Fig. 2(a) and (b)). This indicates the thermal stability of the compounds.

3.2. X-ray diffraction analysis of LiCoO$_2$ and LiMn$_2$O$_4$

The X-ray diffraction profiles of the LiCoO$_2$ and LiMnO$_2$ samples treated at various temperatures are given in Fig. 3(a) and (b), respectively. Though the compound formation is believed to occur at a relatively lower temperature (<400 °C), the ubiquitous presence of carbon contamination is observed. At 400 °C, however, samples are found to be pure and well-crystallized (Fig. 3(a)) Bragg peaks of the heat-treated samples (400 to 700 °C) invariably have constant '*d*' values as well as constant '*a*' and '*c*' values.

Therefore, it is understood that a temperature of 400 °C is the minimum value required for the formation of a single phase product. The degree crystallinity is found to be improved, however, as a function of firing temperature. As the crystallinity is reported to play a vital role in influencing the electrochemical properties of the oxide samples [2], a moderate temperature of at least 700 °C is considered to be essential for a better performing cathode material. The same has been verified from cyclic voltammetric studies, which will be discussed later.

All the X-ray diffraction peaks are indexed assuming a rhombohedral structure for LiCoO$_2$ (sp. gr: *R-3m–D$_{3d}^5$*) and cubic structure for LiMn$_2$O$_4$ (sp. gr: *Fd3m–O$_h^7$*). The crystal constants are determined by an iterative least-squares refinement method using the indexed "*h, k, l*" values and are included in Table 1. The average crystallite size (*D*) of the compounds are calculated using full width at half maximum (FWHM) values of the four main peaks from the Scherrer formula:

$$D = \frac{0.9\lambda}{\beta_r \cos\theta}$$

where λ = X-ray wavelength (Å); θ = Bragg angle (in radians); β_r = FWHM (in radians, values corrected for instrumental line broadening).
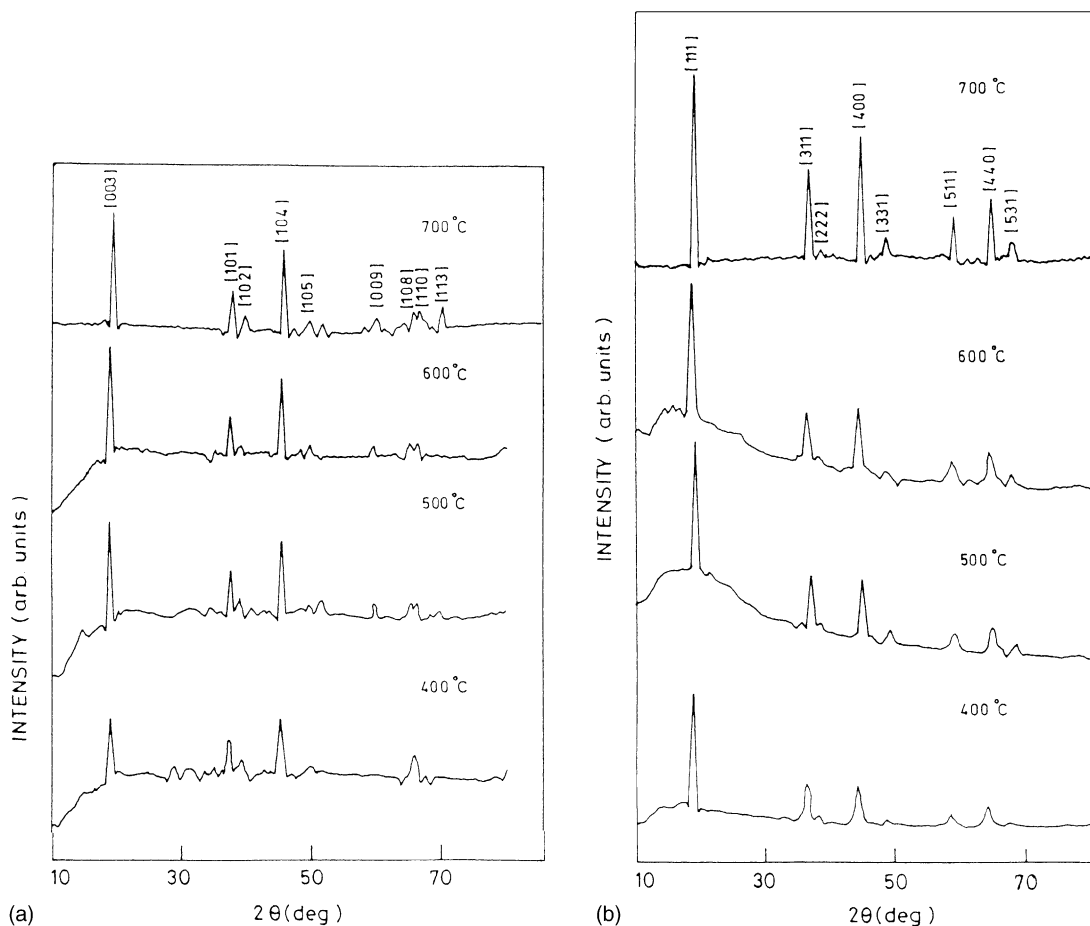
Fig. 3. (a) X-ray diffraction patterns of LiCoO$_2$. (b) X-ray patterns of LiMn$_2$O$_4$.

3.3. FTIR of LiCoO$_2$ and LiMn$_2$O$_4$

Vibrational modes that are attributed to the motion of cations with respect to their oxygen neighbours are sensitive to the point group symmetry of the cations in the oxygen host matrix [10]. Hence, the local environment of the cations in a lattice of close-packed oxygens can be studied by FTIR spectroscopy [11].The FTIR spectrum of LiCoO$_2$ synthesized at 700 °C is given in Fig. 4(a). A band at 615 cm^{-1} ascribed to the asymmetric stretching of Co–O bonds in CoO$_6$ octahedrons and a weak band around 525 cm^{-1} ascribed to the bending modes of O–Co–O bonds [12] are evident from the spectra. This observation is similar to that of Ohzuku et al. [13].

It has been demonstrated that the resonant frequencies of alkali metal cations in their octahedral interstices (LiO$_6$) in inorganic oxides are located in the frequency range of 200–400 cm^{-1} [11,14]. It is generally not possible, however, to assign specific IR frequencies to vibrations which involve a single cation and its oxide neighbours [15], as the resultant vibrations of any transition metal oxide involve contributions from all possible atoms. Moreover, it is only the differences in mass, charge and covalency of lithium and the transition metal cation that lead to the motion of lithium ions and the respective vibrational spectrum [16]. Besides, it is customary that the middle frequency region of FTIR is mainly considered for the analysis, and hence the present study is restricted to the assignment of various vibrational

Table 1
Physical parameters of LiCoO$_2$ and LiMn$_2$O$_4$ derived from SAC process

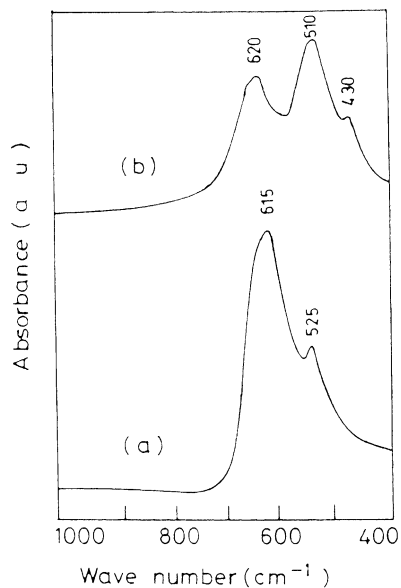| Compound	Crystal constant			Density (g cm^{-3})		Particle-size (Å)		BET surface area (m^2 g^{-1})
	a (Å)	c (Å)	Volume (Å^3)	Observed	Calculated	FWHM	LD[a] (μm)	
LiCoO$_2$	2.812	14.01	95.94	4.15	5.06	0.125	<1.5	15
LiMn$_2$O$_4$	8.21	–	553.4	3.17	4.34	0.035	<1.5	18

[a] Laser diffraction.

Fig. 4. Room temperature FTIR spectrum of (a) $LiCoO_2$ and (b) $LiMn_2O_4$.

modes of transition metal oxide cathodes within the frequency range 400–1000 cm^{-1}. The FTIR spectra of $LiMn_2O_4$ synthesized at 700 °C is shown in Fig. 4(b). The observed high-frequency bands, located around 620 and 510 cm^{-1}, are associated with the asymmetric stretching modes of the MnO_6 group. A weak band at 430 cm^{-1} is due to the vibrations of LiO_4 tetrahedra. These findings are quite similar to those given in earlier reports [17,18].

3.4. Microstructure, particle-size and distribution of $LiCoO_2$ and $LiMn_2O_4$

$LiMn_2O_4$ and $LiCoO_2$ samples heat-treated at various temperatures were obtained powder that contained uniformly distributed and growth-controlled grains. In other words, no significant grain growth or agglomeration of particles was observed as the firing temperature was increased from 400 to 700 °C. From this, it may be concluded that the combustion with starch is not a spontaneous or rapid process, rather it is considered to be a slow process which gives rise to an enormous amount of CO_2 gas and renders the products soft and fluffy. The escaping CO_2 gas dissipates the excess heat that is liberated during combustion and this results in the formation of finer particles. Scanning electron micrographs of the compounds treated at 700 °C are presented in Fig. 5. The plate-like morphology of $LiCoO_2$ (Fig 5(a)) and cube-like morphology of $LiMn_2O_4$ with suppressed grain growth are clearly seen in the micrographs.

A single and a narrow band observed in the lowest particle-size range (<1.2–1.6 μm) for both the compounds is evidence for the mono-dispersed nature of the synthesized particles (Fig. 5(a) and (b)). Such uniformity in size and shape of the crystallites could possibly be due to the homogeneity of the starch–nitrate precursor [19]. Both oxide
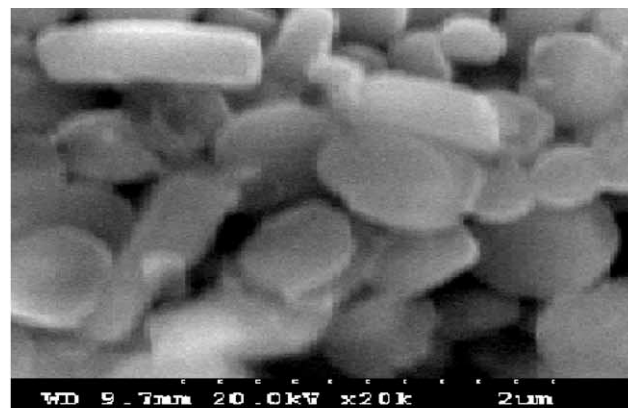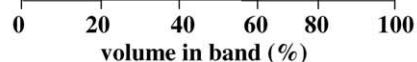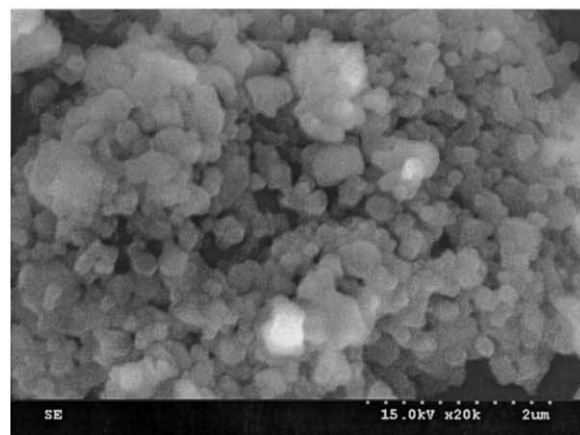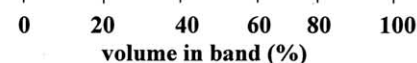

Fig. 5. (a) Microstructure and particle-size distribution of $LiCoO_2$. (b) Microstructure and particle-size distribution of $LiMn_2O_4$.

samples have a specific surface-area between 15 and 18 $m^2\,g^{-1}$, which is quite high when compared with the samples processed by the ceramic route [20]. Physical properties such as smaller particle-size, larger surface-area, growth-controlled particles of uniform size and morphology are reported to be desirable [6,21] for any cathode material in view of better electrochemical behaviour. Interestingly, the same is observed in the present study also.

Materials derived from the combustion method generally have lower density [22] because of the fluffy nature of the products. This is corroborated with the estimated powder density of the samples, which is 70–85% of the theoretical density. Atom absorption spectroscopic analysis reveals that the oxides have close to the ideal composition. The crystal constant values derived from X-ray diffraction analysis and other physical parameters such as density, particle-size and surface-area are given in Table 1.

3.5. Electrochemical studies

The cyclic voltammograms of the compounds synthesized at 400 and 700 °C and cycled between 3.5 and 4.3 V at a scan rate of 0.1 mV s^{-1} are depicted in Fig. 6. Both LiCoO$_2$ and LiMn$_2$O$_4$ are found to exhibit reversibility with respect to Li$^+$ ions, irrespective of the temperature at which the compounds have been prepared. An anodic peak at 4.2 V for LiCoO$_2$ and a broad peak around 4.1 V for LiMn$_2$O$_4$, which are normally attributed to Li$^+$ de-intercalation are observed for the samples treated at 700 °C only. Typical cathodic humps (ascribed to Li$^+$ re-intercalation) occurring around 4.0 and 3.8 V are missing for the samples prepared at 400 °C, an indication that facile Li$^+$ intercalation prefers samples heat-treated at a moderate temperature, say 700 °C. Also, higher peak currents, better cycling behaviour and
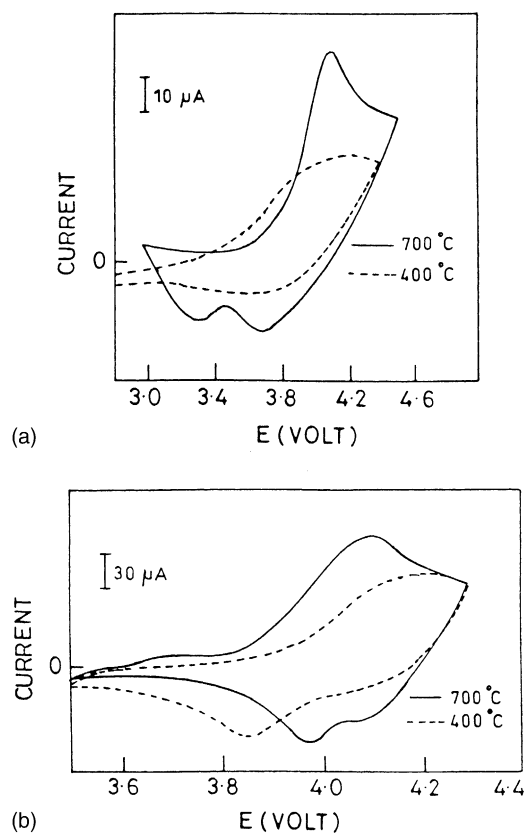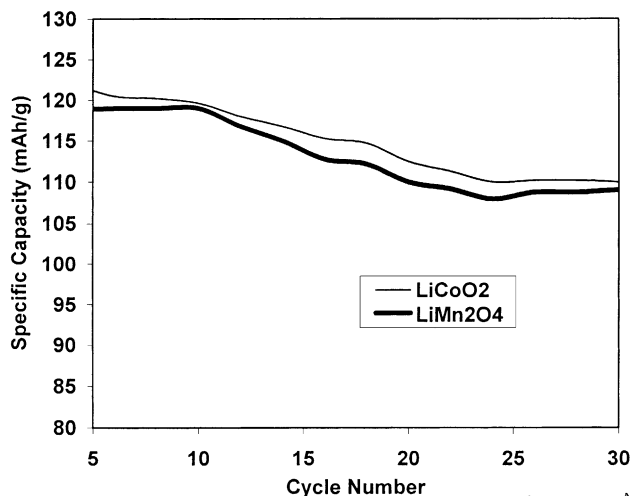

Fig. 7. Capacity vs. cycle number of LiCoO$_2$ and LiMn$_2$O$_4$.

capacity retention are observed for the samples treated at 700 °C only. Hence, it is understood that the electrochemical performance of any electrode material has an unavoidable dependence on the crystallinity of the samples, a factor which coincides with that observed by Spahr et al. [2].

Cycling studies for the samples heat-treated at 700 °C were performed between 3 and 4.2 V at a constant charge–discharge current of 0.1 mA cm^{-2} 2016 type coin cells. The variation in the observed specific capacity with cycle number is shown in Fig. 7. First discharge capacities of about 123 and 12 mAh g^{-1} were obtained for LiCoO$_2$ and LiMn$_2$O$_4$, respectively. At the end of the 30th cycle, discharge capacities of the order of 110 mA g^{-1} for LiCoO$_2$ and 110 Ah g^{-1} for LiMn$_2$O$_4$ were obtained. Thus, upon cycling, a capacity fade of <10% invariably occurs for both the oxides up to 30 cycles. The effect of crystallinity on the electrochemical performance of the cathode materials has been established in a better way from the charge–discharge studies, as is evident from the satisfactory electrochemical behaviour of LiCoO$_2$ and LiMn$_2$O$_4$ synthesized at 700 °C.

4. Conclusions

In this paper, a low-temperature method, namely, the Starch-Assisted Combustion (SAC) method, has been described for the synthesis of the 4 V cathodes *viz.*, LiCoO$_2$ and LiMn$_2$O$_4$. With the use of starch as the combustion-assisting component, high phase purity is achieved at a temperature as low as 400 °C and increased crystallinity is achieved around 700 °C for both the compounds. Scanning electron microscopic indicates mono-dispersed particles of uniform size. The role of heat-treatment temperature in view of better Li$^+$ intercalation/de-intercalation into/from the crystal lattice and the dependence of lithium reversibility on crystallinity has been made obvious from cyclic voltammetric and charge–discharge studies. From the success of this method, we suggest that this methodology, which

Fig. 6. (a) Cyclic voltammogram of LiCoO$_2$ (sweep rate = 0.1 mV s^{-1} (b) Cyclic voltammogram of LiMn$_2$O$_4$ (sweep rate = 0.1 mV s^{-1}).

combines economy-based synthesis and better electrochemical performance, is an ideal choice for any transition metal oxide cathode material. To establish the flexibility of this method, complete solid solutions of $LiCoO_2$ and $LiNiO_2$ have also been synthesized and their electrochemical studies are progressing. Besides, certain experiments are being conducted to synthesize nano-particles using starch alone and in combination with polymers.

Acknowledgements

References

[1] G. Pistoia (Ed.), Lithium Batteries, New Materials, Developments and Perspectives, Elsevier, NY, 1994.

[2] M.E. Spahr, P. Novak, B. Schnyder, O. Haas, R. Nesper, J. Electrochem. Soc. 145 (1998) 1113.

[3] K. Mizushima, P.C. Jones, P.J. Wiseman, J.B. Goodenough, Mater. Res. Bull. 15 (1980) 783.

[4] T. Ohzuku, M. Kitagawa, T. Hirai, J. Electrochem. Soc. 137 (1990) 769.

[5] T. Ohzuku, A. Ueda, M. Nagayama, J. Electrochem. Soc. 140 (1993) 1862.

[6] P. Barboux, J.M. Tarascon, F.K. Shokoohi, J. Solid State Chem. 94 (1991) 185.

[7] T. Sang, A. Manthiram, Solid State Ionics 89 (1996) 30.

[8] P. Kalyani, N. Kalaiselvi, N. Muniyandi, Mater. Chem. Phys., in press.

[9] D. Bloor, R.J. Brook, M.C. Flemings, S. Mahajan (Eds.), The Encyclopedia of Advanced Materials, Vol. 2, Pergamon Press, UK, 1994, p. 864.

[10] C.J. Rougier, G.A. Nazri, C. Julien, Mater. Res. Soc. Symp. Proc. 453 (1997) 647.

[11] A. Rouier, G.A. Nazri, C. Julien, Ionics 3 (1997) 170.

[12] C. Julien, M.A. Camacho-Lopez, T. Mohan, S. Chitra, P. Kalyani, S. Gopukumar, Solid State Ionics 135 (2000) 241.

[13] T. Ohzuku, A. Ueda, M. Nagayama, Y. Iwakoshi, H. Komori, Electrochim. Acta 38 (1993) 1159.

[14] J. Preudhomme, P. Tarte, Spectrochim. Acta 26A (1970) 747.

[15] J. Himmrich, H.D. Lutz, Solid State Commun. 79 (1991) 447.

[16] P. Tarte, A. Rulmont, M. Leigeois-Duyclaerts, R. Cahay, J.M. Winand, Solid State Ionics 42 (1990) 177.

[17] T.J. Richardson, P.N. Ross, Mater. Res. Bull. 31 (1996) 935.

[18] S. Chitra, P. Kalyani, T. Mohan, M. Massot, S. Ziolkiewicz, R. Gangadharan, M. Eddrief, C. Julien, Ionics 4 (1998) 1.

[19] T. Takada, H. Hayakawa, E. Akiba, F. Izumi, B.C. Chakoumakos, J. Power Sources 68 (1997) 613.

[20] H.J. Kweon, G.B. Kim, H.S. Lim, S.S. Nam, D.G. Parks, J. Power Sources 83 (1999) 84.

[21] W. Li, J.C. Curie, J. Electrochem. Soc. 144 (1997) 2273.

[22] M. Kottaisamy, D. Jeyakumar, R. Jagannathan, N. Mohan Rao, Mater. Res. Bull. 31 (1996) 1013.